

N64 11802A
A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

Progress Report 33 for the Period
October 4, 1963 to November 3, 1963

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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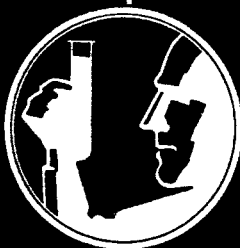
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National Aeronautics and Space Administration
Huntsville, Alabama

Project 1259, Report 33

(2)
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Organic Section

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ABSTRACT

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The investigation of N-alkali derivatives of cyclic silazanes was continued with attempts to form N-alkyl silazanes. No pure products were obtained, and part of the alkyl iodide used was reduced to the corresponding hydrocarbon. This does not appear to be a promising method of synthesis.

Triethylamine was found to have a desirable influence on the reaction of diphenyldichlorosilane with ammonia. The presence of triethylamine evidently favors polymerization in contrast to cyclization and causes the so-called "hexaphenylcyclotrisilazane by-product", which is useful in coatings, to be the major product.

The study of compounds with Si-N-Si units joined by phenylene groups was continued. Encouraging results were obtained with polymers made from starting materials in which methyl groups were attached to the silicon atoms and either methyl groups or hydrogen atoms attached to the nitrogen atoms. In both cases, the thermal stability was good.

Two new polymers with interesting properties were produced from methylphenyldichlorosilane. Reaction with methylamine followed by reaction with hydroquinone produced a tough flexible polymer; reaction with aniline followed by prolonged heating in air produced a polymer that was less tough but that recovered faster after deformation.

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II. POTASSIUM DERIVATIVES OF SILAZANES AS INTERMEDIATES FOR SYNTHESIS

A. Discussion

The N-potassium derivatives of hexaphenylcyclotrisilazane offered a possibility for making specific N-alkyl derivatives that might be useful as lubricants or hydraulic fluids. Previous attempts to make derivatives of this type were described in Report 32; the net result was that no pure N-alkyl derivatives were obtained. A small amount of additional work has been done on N-octadecyl and N-decyl derivatives with the same result. It appears that the N-potassium or N-alkyl derivatives are subject to disproportionation, and so this does not seem to be a promising route to new useful materials. However, other N-metal derivatives will be tried.

B. Experimental Details

1. Attempt to prepare an octadecyl derivative of hexaphenylcyclotrisilazane

In a 200-ml, 3-neck round-bottom flask fitted with a thermometer, reflux condenser, magnetic stirrer, and dropping funnel were placed 30 ml of purified dioxane and 2.18 g (0.0558 mole) of potassium. The flask was flushed with nitrogen, the liquid was heated with stirring to 60°C, and hexaphenylcyclotrisilazane, 10.0 g (0.0169 mole) dissolved in 50 ml of dioxane, was added. The mixture was refluxed for 4 hours which caused all but a trace of the potassium to dissolve. The liquid was cooled to room temperature, and 21.03 g (0.0553 mole) of 1-iodooctadecane in 50 ml of dioxane was added, whereupon the temperature rose 8°C. The mixture

was then stirred at 36-38°C for 2 hours. A large amount of solid, presumably potassium iodide, appeared in the solution. The product was cooled and filtered, and the precipitate was washed with dioxane. When free of solvent, the precipitate weighed 7.35 g (80% of the theoretical amount of potassium iodide).

The dioxane was distilled from the filtrate at reduced pressure, and the residue was a tan solid in a red-orange liquid. The suspension was filtered, and the solid portion was found to weigh 8.3 g. When an attempt was made to determine its melting point, it appeared to decompose at 160-165°C. An attempt was made to distill the liquid. Part of it distilled at 105-119°C at 0.1 mm, and carbon-hydrogen analysis indicated that the distillate was largely a hydrocarbon. The remainder was a soft solid. It was apparent that the reaction was complex and that no appreciable amount of a liquid derivative of hexaphenylcyclotrisilazane was produced. Hence, no further work was done on the octadecyl derivative.

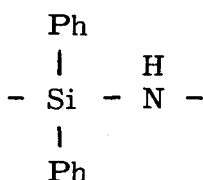
2. Attempt to prepare a decyl derivative of hexaphenylcyclotrisilazane

Potassium and n-decyl iodide were used in an attempt to prepare a decyl derivative of hexaphenylcyclotrisilazane. The method and results were similar to those just described.

III. IMPROVED METHOD OF PREPARING MATERIAL EQUIVALENT TO THE HEXAPHENYLCYCLOTRISILAZANE BY-PRODUCT

A. Discussion

A polymeric by-product obtained in the preparation of hexaphenylcyclotrisilazane was reported as a promising coating agent for high-temperature use.¹ Recently a method of increasing the yield of the "by-product" from 17% to more than 90% has been found. The reaction of diphenyldichlorosilane with ammonia in benzene normally produced yields of about 75% hexaphenylcyclotrisilazane and 17% by-product. By running the reaction in the presence of triethylamine, the yield of by-product was increased to 90% or more, and it was not necessary to remove hexaphenylcyclotrisilazane, if any were present. The product made in the presence of triethylamine is called the "polymeric diphenylsilazane." It and the hexaphenylcyclotrisilazane by-product are believed to be low-molecular-weight polymers with this repeating unit:



Both the hexaphenylcyclotrisilazane by-product and the polymeric diphenylsilazane form protective coatings of good stability when heated alone. However, they form more flexible coatings when heated with 10% by weight of ethylenediamine silazane. Such coatings require curing at about 300°C. They are flexible and still protect a metal substrate from hydrochloric acid after being heated in air at 400°C for 20 hours.

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1. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 58-60 and 61-64.

B. Experimental Details

One of three preparations of polymeric diphenylsilazane was carried out as follows: In a 500-ml, 3-neck, round-bottom flask fitted with a stirrer, dropping funnel, reflux condenser, and gas inlet tube were placed 300 ml of benzene and 39.05 ml (28.23 g, 0.279 mole) of triethylamine that had been purified by distillation from phthalic anhydride and then from potassium hydroxide. Then 28.90 ml (35.32 g, 0.139 mole) of diphenyldichlorosilane was added dropwise with stirring. The mixture became thick and cloudy. Then for 2.5 hours ammonia was passed over the surface of the mixture as it was being stirred. The temperature rose to 40°C and then returned to room temperature. The absorption of ammonia was indicated by a rubber balloon attached to the top of the condenser. After the mixture had stood overnight, the Beilstein Test for halogens was positive; so introduction of ammonia was resumed for 2 hours. The mixture was heated while stirring to 80°C and then allowed to cool. The salts were removed by centrifugation, and the solid was washed with benzene. The solvent was removed by distillation at the reduced pressure provided by a water aspirator; the final pot temperature was 87°C. The cloudy, tan, viscous liquid product weighed 25.9 g, which was 94.1% of the theoretical yield when $-\text{Si}(\text{Ph})_2\text{NH}-$ was assumed as the formula of the product.

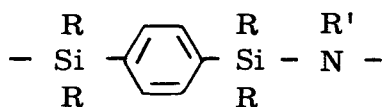
Two other reactions were run with different proportions of triethylamine. In one reaction, triethylamine was the solvent; in the other, the mole ratio of triethylamine to diphenyldichlorosilane was 1:1.

When triethylamine was the solvent, diphenyldichlorosilane, 35.32 g (0.140 mole) was added to 300 ml (216.9 g, 2.14 moles) of triethylamine, and then ammonia was passed in as described above. The yield was 25.8 g, 93.7% of theoretical when $-\text{Si}(\text{Ph})_2\text{NH}-$ was assumed as the formula of the product.

In the reaction with 1:1 mole ratio, diphenyldichlorosilane, 35.32 g (0.140 mole) was added to 19.52 ml (14.11 g, 0.140 mole) of triethylamine in 300 ml of benzene, and then the ammonia was passed in as before. The yield was 27.1 g, 98.4% of theoretical when $-\text{Si}(\text{Ph})_2\text{NH}-$ was assumed as the formula of the product.

IV. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

The derivatives of 1,4-bis(dimethylchlorosilyl)benzene that have been made are represented by the following formula:



R = methyl or phenyl

R' = methyl or hydrogen

The derivative in which R was methyl and R' was hydrogen polymerized when heated at 250°C overnight while nitrogen was bubbled through it to produce a product that was a fairly-tough, white solid at ordinary temperatures. This material was liquid at 190°C, so it may be capable of further polymerization, and it was soluble in benzene. A short study of its coating properties indicated that it had good adhesion, flexibility, and stability.

The preceding report, Report 32, described a tough, red-brown elastomer that was made from the derivative in which both R and R' were methyl. In additional experiments this derivative was heated with air bubbling through it for 16 hours at 250°C. It polymerized to a dark-yellow, viscous liquid that was then tried as a vehicle for a pigmented coating. The polymer, 1 part, was dissolved in benzene, 9 parts, and then mixed with aluminum powder, 0.1 part. The suspension was spread evenly on a stainless-steel panel, and the benzene was allowed to evaporate. The panel was heated at 400°C for 30 minutes and at 600°C for 30 minutes. The coating remained in place, and it could not be scratched with a fingernail. After the panel was bent over a mandrel with a radius of 4 mm, the coating could be scratched where it had been bent. The coating was not an electrical insulator. Consequently, there is some question whether the organic part of the vehicle was still present.

The investigation of these polymers and coatings is being continued.

V. POLYMERS FROM METHYLPHENYLDICHLOROSILANE

A. Discussion

The preceding report described a resilient polymer made by mixing 9 parts of methylphenylsilazane with 1 part of ethylenediamine silazane and heating the mixture in air. The promising properties of this polymer encouraged further work on derivatives of methylphenyldichlorosilane.

Treatment of methylphenyldichlorosilane with methylamine produced a yellow, cloudy liquid. In an attempt to increase the degree of polymerization, the liquid was heated at 160°-170°C with ammonium chloride, which is known to be a catalyst for rearranging Si-N bonds. The viscosity of the liquid increased slightly, but no significant amount of polymerization was obtained. The product formed brittle coatings that adhered poorly to aluminum. On heating the yellow liquid with hydroquinone, a hard, black solid with a low softening point was obtained. The yellow liquid was distilled, and a purer product was obtained that was probably a mixture of bis(methylamino)methylphenylsilane and the corresponding four-membered ring compound. An interesting polymer was produced when the distilled product was treated with hydroquinone. This polymer was a tough elastic material that became stiff on standing, but became soft and flexible when flexed. Prolonged heating at 350°C caused the flexible plastic to become hard.

Methylphenyldichlorosilane reacted with aniline to produce a dark-colored, semicrystalline material that is now being purified. Heating the crude product at 190°C for 65 hours produced a fairly-tough, elastic polymer that was smooth, homogeneous, and black. It retained some of its elasticity after 60 minutes at 425°C, whereas Viton A became hard in 15 minutes.

B. Experimental Details

1. Methylamine derivatives of methylphenyldichlorosilane

a. Preparation of "methylphenyl methylamino silazane"

Methylphenyldichlorosilane in benzene was treated with methylamine in the usual way. Details were given in Report 32, page 29, for a similar reaction with ammonia. The product was a cloudy, yellow, viscous liquid called the "methylphenyl methylamino silazane."

b. Attempt to polymerize with ammonium chloride as the catalyst

The methylphenyl methylamino silazane, 4.0 g, was stirred in a nitrogen atmosphere with 0.1 g of ammonium chloride at 160-170°C for 7 hours. No increase in viscosity was observed. Consequently, another 0.1 g of ammonium chloride was added, and heating was continued for 7 hours. The product was only slightly more viscous than at the start of the reaction. Methylamine was detectable by odor throughout the reaction, and the rate of evolution appeared to decrease near the end. Attempts to make coatings with the product on aluminum led to brittle, flaky films that did not encourage further effort.

c. Reaction with hydroquinone

The methylphenyl methylamino silazane, 8.9 g [0.06 mole, if the compound was bis(methylamino)methylphenylsilane] was mixed with 6.6 g (0.06 mole) of hydroquinone, and a rapid reaction occurred. The mass was stirred at 260-270°C for 4 hours. A small part of the resulting liquid was heated on a panel, but the film formed was brittle and had poor adhesion. The liquid polymerized further in 2 hours at 300-310°C, and then brittle fibers could be pulled from the melt as it cooled to a hard solid.

d. Distillation of methylphenyl methylamino silazane and reaction with hydroquinone

The yellow, viscous methylphenyl methylamino silazane was distilled in a 1.2 x 30-cm packed column, and the following fractions were obtained:

1. B. p. 67-68°C at 1.5 mm, 2.6 g, clear liquid
2. B. p. 68°C at 1.5 mm, 23.4 g, clear liquid
3. B. p. 68°C at 1.5 mm, 7.8 g, clear liquid
4. Residue, did not distill at 168°C at 1.5 mm; 11.8 g, brown solid when cool

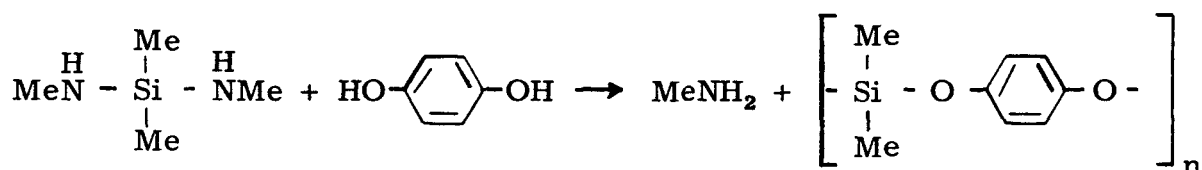
Fraction 2 was expected to be bis(methylamino)methylphenylsilane. It did not crystallize even when scratched with a glass rod at temperatures down to -80°C. Its neutral equivalent was 95.7 (theoretical, 90.16). Its elemental composition was:

Found: Carbon, 59.87%; hydrogen, 8.08%; nitrogen, 15.79%; silicon, 14.8% (total, 98.54%)

Calculated: Carbon, 59.94%; hydrogen, 8.94%; nitrogen, 15.54%; silicon, 15.58%

Its molecular weight by vapor osmometry as determined by Galbraith Laboratories, Inc., was 253 (average of 264 and 242); calculated 180.3. These data show that the product was not pure bis(methylamino)methylphenylsilane.

A portion of Fraction 2, 8.9 g (0.06 mole if purity was assumed) was dissolved in 20 ml of tetrahydrofuran and 6.6 g (0.06 mole) of hydroquinone in 40 ml of tetrahydrofuran was added dropwise with stirring. Methylamine was evolved. The solution was refluxed for 4 hours, then the solvent was distilled off at reduced pressure to leave 13.9 g (102% of theory) of a viscous red-orange liquid. The expected reaction was:



The red-orange liquid product was heated for 18 hours at 190°C in a Teflon beaker. The product was a small black disc, 5-mm thick and 20 mm in diameter, that was tough, pliable, and elastic. It became fairly rigid on standing for several hours, but pliability returned when it was flexed. After a small strip if it was heated in air at 350°C for an hour, it was still flexible. Heating at 450°C for 1.5 hour made it hard and brittle.

2. Aniline derivatives of methylphenyldichlorosilane

To determine whether an aniline derivative of methylphenyldichlorosilane might polymerize better than a methylamine derivative, methylphenyldichlorosilane, 95.5 g (0.50 mole), was dissolved in 30 ml of benzene and added dropwise to 465.6 g (5.0 moles) of aniline in 250 ml of benzene. The solution was refluxed for 4 hours, and the precipitate was filtered off. The benzene and excess aniline were distilled at reduced pressure and a viscous, red-brown liquid, 125.1 g (82% of theory), was obtained as the product. After standing for 3 days, it was partially crystalline.

A portion of the crude mixture was heated in air in a Teflon beaker at 185°C for 3 days. About two-thirds of it evaporated, but the remainder was a smooth, 1 mm thick, homogeneous, resilient black polymer, that was fairly tough. Samples of it and of Viton A were heated in air at 425°C. The Viton A became hard in 15 minutes while the methylphenyl derivative still retained some resilience after an hour.

The rest of the mixture is now being recrystallized.

VI. ANTICIPATED WORK

Work on materials made from methylphenyldichlorosilane is promising enough to be continued. Variations in the method of making the elastomer by heating the aniline reaction product in air will be studied. The reaction of the methylamine and aniline derivatives with difunctional aromatic compounds will also be studied.

The study of organometallic derivatives of silazanes will begin with a study of the reaction of metal alkoxides with silazanes. Later it may be necessary to react metal halides with alkali derivatives of silazanes.

The study of steric factors to inhibit cyclization will be studied principally through the effects of tertiary amines on the reaction of chlorosilanes with amines. Attempts will be made also to determine whether phthalocyaninodichlorosilane can be made to form linear polymers with ammonia.

Attempts to make gaskets and pigmented protective coatings from the aromatic-bridge compounds will be continued.

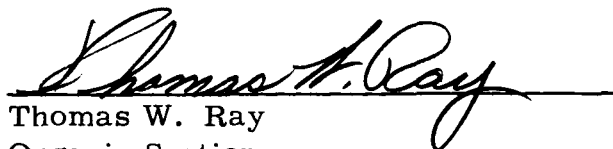
VII. TIME EXPENDITURE

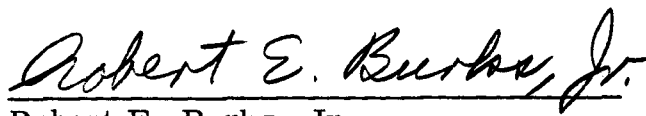
The time expenditure during the monthly period covered by this report was 721.5 man-hours. The time expenditure during the preceding six months was 4091.0 man-hours.

ACKNOWLEDGMENTS


Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist and Mr. Charles L. Christy, Jr., Chemical Technician, assisted with the laboratory work.

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Total	27

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- 1.1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B.1.b)
2. Elastomers - silyl derivatives of ethylenediamine (see B.7)
3. Structural plastics

1. **Metalation of silylamines as a method of synthesis**
 - a. Polymers
 - b. Lubricants (see A. 1)
 - c. Organometallics
2. **Polymerization of cyclic silazanes at high temperatures and pressures**
3. **Condensation polymerization of silylamines with difunctional aromatic compounds**
4. **Steric factors to inhibit cyclization**
5. **Polyethylenimine as a source of silicon-nitrogen polymers**
6. **Properties of methylhydrogen silazanes**
7. **Elastomers from ethylenediamine silazanes (see A. 2)**
8. **Addition of silicon tetrafluoride to silazanes and amines**
9. **Heats of combustion as indicators of aromaticity**
9. **Polymers from methyltrichlorosilane and silicon tetrachloride**
 1. Silicon-nitrogen compounds with aromatic bridges
 2. Factors affecting hydrolytic and thermal stabilities

D. Applications - Search for New Uses

F. Preparation of Final Report

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.